Russian Journal of General Chemistry 2004 vol.74 N6, pages 864-872

Synthesis and hydrophosphorylation of π-complexes of Esters of unsaturated carboxylic acids with chromium subgroup metals

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Abstract

Photochemical and thermochemical activation were used to prepare new π-complexes of chromium, molybdenum and tungsten containing η 2- and η 4-coordinated methyl acrylate, methyl cynnamate, and dimethyl fumarate molecules. Geometric, electronic, and energetic parameters of the coordinated ester molecules were found and factors governing η 2- and η 4-coordination of the oxodiene system were revealed by nonempirical calculations. Monocarboxylic acid esters incorporated in the π-complexes react with dialkyl hydrogen phosphites to give dialkyl acyl phosphites coordinated with the metal center and susceptible to oxidation the corresponding phosphates. In this case, the phosphorylation involves the OH-tautomer of dialkyl hydrogen phosphite. Coordinated dimethyl fumarate undergoes phosphorylation by two concurrent pathways, viz. transesterification or Pudovik reaction. In the latter case, fragmentation of the organometallic compound takes place.

http://dx.doi.org/10.1023/B:RUGC.0000042421.46358.cd